Laid-open Application No. JP56-104802A dated August 20, 1981
Applicant: Montedison S.p.A.
Title: Solid formulations containing pheromones

[Claims]

(1) A solid formulation, comprising: an insect sex pheromone as an active substance, supported on an inert material coated with a film-forming resin, a wetting agent, a dispersant and an adhesive agent, an ultraviolet stabilizer, and an antioxidant, the formulation having the following composition:

A	Active substance - sex pheromone	0.5 to 10wt%
B	Film-forming resin	5 to 30wt%
C	Dispersant - wetting agent - bonding agent	5 to15wt%
D	U.V. Stabilizer	0.5 to 10wt%
E	Antioxidant	0.5 to10wt%
F	Inert carrier	balance to 100wt%

(2) The formulation according to claim 1, wherein the active substance is preferably used in an amount of about 5%.

(3). The formulation according to claim 1, wherein the active substance is (Z,E)-9,11-tetradecadienyl acetate, i.e. pheromone of Spodoptera littoralis.

(4) The formulation according to claim 1, wherein the active substance is (E,E)-8,10-dodecadienol, i.e. pheromone of Laspeyresia pomonella.

(5) The formulation according to claim 1, wherein the active substance is (Z)-11-hexadecenal, i.e. pheromone of Heliothis armigera.

(6) The formulation according to claim 1, wherein the active substance is (E)-11-tetradecenal, i.e. pheromone of Choristoneura fumiferana.

(7) The formulation according to claim 1, wherein the film-forming resin used is a mixture of chlorinated derivatives of terpene polymers or of natural rubber.

(8) The formulation according to claim 4, wherein the film-forming

resin is preferably used in an amount of about 15 to 25%.

(9) The formulation according to claim 1, wherein the ultraviolet stabilizer is a 2-hydroxy-4-alkoxybenzophenone derivative, preferably 2-hydroxy-4'-octyloxybenzophenone.

(10) The formulation according to claim 1, wherein the antioxidant is a 2,6-di-tert-butylphenol derivative, preferably pentaerythrite 2,6-di-tert-butylphenol propionate or stearyl 2,6-di-tert-butylphenol propionate.

(11) The formulation according to claim 1, comprising:

A	Active substance	5wt%
B	Film-forming resin	15wt%
C	Dispersant	5wt%
D	Adhesive agent	5wt%
E	U.V. Stabilizer	5wt%
F	Antioxidant	5wt%
G	Inert substance	55wt%

(12) The formulation according to claim 1, comprising:

A	Active substance	5wt%
B	Film-forming resin	30wt%
C	Dispersant	5wt%
D	Adhesive agent	10wt%
E	U.V. Stabilizer	5wt%
F	Antioxidant	5wt%
G	Inert substance	40wt%

(13) The formulation according to claim 1, comprising:

A	Active substance	5wt%
B	Film-forming resin	20wt%
C	Dispersant	5wt%
D	Adhesive agent	10wt%
E	U.V. Stabilizer	5wt%
F	Antioxidant	5wt%
G	Inert substance	50wt%

(14) The formulation according to claim 1, in the form of a wettable powder.

(15) A method for suppressing harmful insects, characterized by distributing through an infested area the formulation according to claim 1, either as is or in the form of a wettable powder.

The main inert materials on which the active principle is supported, are, for instance: calcined fossil meal, kaolin, micronized attapulgites, talc and the like. The fossil meal has a composition based on Al, Fe, Ca, Mg, Na, K silicates. Typical examples are: "Celite SCC", and "Celite 209". Kaolin has a composition mainly based on aluminum silicate; a typical example is "Argirek B22". Attapulgites have compositions based on Al, Mg, Ca, Fe, Na, K silicates; a typical example is "Diluex".

As a special advantage, these formulations with controlled release can be applied by the methods and with the equipment usual for wettable powders, with quite appreciable economical advantages, so that they can be easily handled by any user.

The examples below are illustrated for better explaining the invention.

Example 1

This example illustrates the tests performed for selecting the most adequate stabilizer.

100 g of the compositions from 1 to 10 given in Table I were prepared by depositing, from a solution in CH_2Cl_2, the active substance (henceforth called a.s.) and usable stabilizers on a pre-selected carrier, and by subsequently allowing the solvent to evaporate.

50 g of such compositions were maintained for 14 days at room temperature, and 50 g of the compositions were kept at a thermostatically stabilized temperature of 40°C. At the end of this period, the residual active substance, after extraction with n-hexane, was evaluated by gas-liquid chromatography.

Table I

Components	Composition									
	1	2	3	4	5	6	7	8	9	10
(Z,E)-9,11 C_{14} A_C (a.s.) (1)	5	5	5	5	5	5	5	5	5	5
Clortex 70 (2)	95			15			15			
Vinavil C4 (3)		95			15					
Picolite S85 (4)			95			15		15		
UV 531 (5)							5	5		5
Irganox 1010 (6)							5	5		5
Celite SSC (7)				80	80	80	70	70	95	85
Degradation % after	9.1	12.3	6.2	24.8	31.4	7.3	<0.1	<0.1	83	<0.1

14 days at: Room temp.										
40°C	23.6	33.5	18.4	28.2	35.2	10.1	<0.1	<0.1	82	<0.1

Notes to Table I

(1) Pheromone of Spodoptera littoralis (Z,E)9,11-tetradecadienyl acetate.

(2) "Clortex": registered trademark of Caffaro, mixtures of chlorinated derivatives of natural rubber.

(3) "VINAVIL C4": registered trademark of Montedison, carboxylated polyvinylalcohols.

(4) "Picolite S85": registered trademark of ChemPlast, terpene polymers.

(5) U.V. 531: 2-hydroxy-4-n-octyloxybenzophenone.

(6) "Irganox 1010": pentaerythrite 2,6 di-terbutylphenolpropionate.

(7) "Celite SSC": registered trademark of Johns Manville, fossil meal.

The samples 7, 8 and 10 were subjected to a U.V. radiation test under the following conditions:

- Solar spectrum lamp with emission of U.V. radiation;
- Distance of samples from the lamp = 20 cm;
- Temperature: 40°C.

At different times, part of the sample is drawn and the residual active substance is evaluated, after extraction with n-hexane, by means of gas-liquid chromatography. The results are given in Table II.

Table II

Sample No.	a.s.: residue % after time of exposure minutes		
	0	1440	2280
7	100	67.8	49.6
8	100	66.3	37.8
10	100	44.1	8.0

Example 2

Release tests of (Z,E)-9,11 C_{14} acetate stabilized with Celite SSC and with compositions based on Celite SSC having film-forming coating resin.

100 g of compositions 11, 12 and 13, shown in Table III, were prepared by depositing, from a solution in CH_2Cl_2, the active substance, the

stabilizers and the film-forming resin onto a powdery carrier, and by successively allowing the solvent to evaporate. The samples of Table III were then exposed, in a suitable cell, to the following conditions:
- Temperature: 30°C
- Artificial lighting:15 hours on 24 hours
- Air change:160 m^3/hour corresponding to 6 total changes of the air in the cell per hour.

At different times, drawings from the exposed samples were effected and, after extraction with n-hexane, the percentage of residual active substance was calculated. The results are given in Table III below.

Table III

Components	Compositions		
	11	12	13
(Z,E)-9,11 C_{14} AC	5	5	5
U.V. 531	5	5	5
Irganox 1010	5	5	5
Clortex 70	-	10	-
Picolite S 85	-	-	10
Celite SSC	85	75	75

Table III (cont'd)
Release test data

Sample No.	a.s.: % of residue after time of exposure (hours)						
	0	30	118	169	300	430	500
11	100	93.7	75.8	67.0	41.2	16.8	0.0
12	100	98.1	93.1	94.0	81.5	73.77	70.0
13	100	97.7	88.6	85.3	75.0	68.5	57.3

Example 3
Preparation of Complete Formulations

100 g of formulations 14, 15 and 16, shown in Table IV, were prepared by depositing, from a solution in CH_2Cl_2, the active substance, the stabilizers and the resin onto a powdery carrier. Once the solvent had evaporated at room temperature, the indicated quantities of wetting agent, dispersant and adhesive agent were then admixed. The mixture

was then homogenized by passing through a suitable mechanical mixer.

Table IV

Components	Composition		
	14	15	16
(Z,E)-9,11 C_{14} AC (a.s.)	5	5	5
Irganox 1010	5	5	5
UV 531	5	5	5
Clortex 70	15	30	-
Picolite S85	-	-	20
Reax 45A	5	5	5
Polymer PS50 (RP 10) (2)	10	10	10
Celite SSC	55	40	50
Degradation % after 14 days at: Room temp.	<0.1	<0.1	<0.1
40°C	<0.1	<0.1	<0.1

Notes to Table IV:

(1) Reax 45A: registered trademark of Westvaco, sodium lignosulphonate.

(2) Polymer PS 50 (RP 10): registered trademark of ROL, mixtures of methacrylic polymer and nonylphenolpolyoxyethylate.

Example 4

Release Tests of Complete Formulations

With formulations 14, 15 and 16 there were carried out release tests under the same conditions and following the same procedures as in Example 2. The results thus obtained are given in the following table.

Data of release tests

Sample No.	a.s.: % of residue after time of exposure (hours)						
	0	95	168	264	624	1104	1224
14	100	94.8	91.1	88.3	67.1	37.9	35.3
15	100		94.3		88.1	72.0	
16	100		90.8		79.4	59.5	

Example 5

Confusion Method Test in Egypt

Using formulation 14 of Example 4 there were conducted confusion tests

on Spodoptera littoralis in Egypt, in the Faiyum region, locality Tamiya, for the periods June 8 to June 30, and July 1 to July 6. The formulation was applied on an area of 2 Feddan (1 Feddan=4,200 m^2) cultivated with cotton, with a dose of 4 g of active substance /Feddan.

A 0.2% aqueous suspension of the formulation was applied from the ground by means of a standard sprinkling device.

The effectiveness of the confusion was assessed by comparing the number of adult males captured in 4 traps baited with the same pheromone and placed one pair inside the treated zone and the other pair in the untreated zone (witness) adjacent to the treated zone. The data are given in Table V.

Table V

		8.6.1979	9	10	11	12	13	14 (1)	15	16	17	18	19	20	21
Treated zone	Trap 1	56	103	207	137	268	254	285	0	9	26	84	6	12	14
	Trap 2	36	69	19	93	159	168	382	15	139	98	127	105	55	42
	Total captures	92	172	398	230	427	422	667	15	148	124	221	111	67	56
Witness	Trap 3	51	33	112	89	162	195	448	67	213	195	325	25	4	13
	Trap 4	59	77	216	229	256	147	395	36	394	281	257	246	131	186
	Total captures	110	100	328	318	418	342	843	103	610	476	582	271	135	199
Temperature °C	Max.	35	33	35	37	40	42	40	39	39	40	41	43	43	43
	Min.	21	23	21	22	22	22	23	23	23	22	23	24	25	24
U.R.	%	49	59	42	44	32	36	34	35	38	35	48	42	42	40

Table V (cont'd)

		22	23	24	25	26	27	28	29	30	1.7. 1979	2	3	4	5	6
Treated zone	Trap 1	6	3	5	21	10	1	3	3	2	0	0	3	0	0	0
	Trap 2	0	0	6	28	6	4	7	0	0	0	0	1	0	0	0
	Total captures	6	3	11	49	16	5	10	3	2	0	0	4	0	0	0
Witness	Trap 3	13	12	26	2	11	5	7	0	3	0	0	2	1	3	2
	Trap 4	98	62	45	264	145	38	27	5	12	4	5	7	12	15	16

	Total captures	111	74	71	266	156	43	34	5	15	4	5	9	13	18	18
Temperatur	Max.	42	41	45	45	45	43	43	40	40	39	41	38	41	41	42
e °C	Min.	23	24	26	24	23	22	22	21	22	21	20	21	22	21	21
R.H.	%	46	42	42	52	52	49	48	50	42	42	50	50	44	44	46

(1) Initial day of the treatment, carried out during evening hours

Example 6

The following formulations were prepared following the procedures of Example 3.

Table VI

Components	17	18
(E,E)-8,10 C_{12} OH (1))	5	5
UV 531	5	5
Irganox 1010	5	5
Celite SSC	60	60
Clortex 70	10	-
Picolite S85	-	10
PS50 (RP 10) polymer	10	10
Reax 45A	5	5

Note to Table VI

(1) Pheromone of Laspeyresia pomonella

Release tests were carried out with samples of formulations 17 and 18, under the same conditions and by the same procedures described in Example 2. The results are shown in Table VII.

Table VII

Sample No.	a.s.: % of residue after time of exposure (hours)						
	0	30	96	230	400	660	1260
17	100	99.5	91.7	92.8	82.6	71.7	47.4
18	100	96.4	93.1	92.2	88.4	77.5	56.0

Example 7

Following the same procedures as those indicated in Example 3, there were prepared formulations 19 and 20 in Table VIII.

Table VIII

Components	19	20
(Z)-11-hexadecen-1-al (1)	5	/
(E)-11-tetradecen-1-al (2)	/	5
UV 531	5	5
Irganox 1010	5	5
Celite SSC	55	55
Clortex 70	15	15
PS50 (RP 10) polymer	10	10
Reax 45 A	5	5

Notes to Table VIII:

(1) Pheromone of Heliothis armigera;

(2) Pheromone of Choristoneura fumiferana.

Following the procedures of Example 2, release tests were carried out with formulation No. 19. The results thereby obtained have been recorded in following Table IX.

Table IX

Sample	a.s.: % of residue after time of exposure (hours)					
No.	0	75	195	410	570	875
19	100	93.7	92.1	67.9	64.7	46.6